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Weighting of Fourier series for improvement of efficiency of convergency in crystal analysis: space group *P*1.

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Vand & Pepinsky (1957) have discussed the weighting scheme to be adopted for improving the efficiency of refinement by the Fourier method in the case of a centrosymmetrical crystal structure. They have applied the statistical results of Luzzati (1952) who has considered the effect of errors in atomic coordinates on the distribution of the difference between the observed and calculated structure factors. From purely probability arguments, Vand & Pepinsky have arrived at the following weighting function W for the centrosymmetric case:

$$W = \tanh\left[\frac{|F_o F_c|}{\varphi(1/D - D)}\right] \tag{1}$$

where F_o and F_c are the observed and calculated structure factors, $D = \langle \cos 2\pi \Delta\mathbf{r}.\mathbf{H} \rangle$, $\Delta\mathbf{r}$ being the errors in atomic coordinates, and $\varphi = \sum_{j=1}^{N} f_j^2$. When the errors in atomic coordinates follow a Gaussian law of distribution, the value of D is given by (Luzzati, 1952)

$$D = \exp\left[-2\pi^2\sigma^2 H^2\right], \tag{2}$$

where σ is the standard deviation of the error $\Delta\mathbf{r}$ in atomic coordinates, which can be related to the mean error $\langle|\Delta\mathbf{r}|\rangle$, the formulae for which are given by Luzzati (1952) for one, two, and three dimensions. In practice, one usually estimates the value of D to be used in expression (1) from the available relation between R and D (see Luzzati, 1952, Table 1). Vand & Pepinsky have also suggested some practical improvements to carry out the above procedure for the centrosymmetric case.

The purpose of this note is to derive a corresponding weighting scheme for the non-centrosymmetric case. This can be obtained easily since the basic formulae required are available in Luzzati's paper (1952). Thus, following Blow & Crick (1959), and Sim (1960), the weighting function W to be used in the present case is the mean value of $\cos\gamma$, where γ is the difference in phase angle between the true phase angle α_o and the calculated phase angle α_c. From Luzzati's expressions for the distribution of the difference between the observed and calculated structure factors F_o and F_c it can be shown that for given values of $|F_o|$ and α_c the joint probability that $|F_o|$ lies between $|F_o|$ and $|F_o|+d|F_o|$ and γ lies between γ and $\gamma+d\gamma$ is

$$P(|F_o|, \gamma)\,d|F_o|\,d\gamma = \frac{|F_o|\,d|F_o|}{\pi\varphi(1-D^2)} \exp\left[-\frac{D^2F_c^2 + F_o^2 - 2D|F_c||F_o|\cos\gamma}{\varphi(1-D^2)}\right] d\gamma, \tag{3}$$

where

$$\varphi = \sum_{j=1}^{N} f_j^2 .$$

The probability that $|F_o|$ lies between $|F_o|$ and $|F_o|+d|F_o|$ is then

$$\begin{aligned} P(|F_o|)\,d|F_o| &= \frac{|F_o|\,d|F_o|}{\pi\varphi(1-D^2)} \int_{-\pi}^{\pi} \exp\left[-\frac{D^2F_c^2 + F_o^2 - 2D|F_c||F_o|\cos\gamma}{\varphi(1-D^2)}\right] d\gamma \\ &= 2\frac{|F_o|\,d|F_o|}{\varphi(1-D^2)} \exp\left[-\frac{D^2F_c^2 + F_o^2}{\varphi(1-D^2)}\right] \\ &\quad \times \frac{1}{\pi}\int_0^{\pi} \exp\left[\frac{2D|F_c||F_o|\cos\gamma}{\varphi(1-D^2)}\right] d\gamma \\ &= 2KI_0(X), \end{aligned} \tag{4}$$

where

$$K = \frac{|F_o|\,d|F_o|}{\varphi(1-D^2)} \exp\left[-\frac{D^2F_c^2 + F_o^2}{\varphi(1-D^2)}\right], \tag{5}$$

$$X = \frac{2D|F_c||F_o|}{\varphi(1-D^2)} \tag{6}$$

and $I_0(X)$ is the modified Bessel function of order zero (Watson, 1922). For fixed values of $|F_o|$, $|F_c|$ and α_c

$$P(\gamma)\,d\gamma = \frac{P(|F_o|, \gamma)\,d|F_o|\,d\gamma}{P(|F_o|)\,d|F_o|}. \tag{7}$$

Now the weighting function W is

$$W = \int_{-\pi}^{\pi} \cos\gamma P(\gamma)\,d\gamma .$$

Substituting from equations (3), (4) and (7), we have

$$W = \frac{2K\frac{1}{\pi}\int_0^{\pi} \exp\left[\frac{2D|F_c||F_o|\cos\gamma}{\varphi(1-D^2)}\right] d\gamma}{2KI_0(X)}$$

which reduces to

$$W = I_1(X)/I_0(X)$$

where $I_1(X)$ is the modified Bessel function of order one.

Following Vand & Pepinsky, if we use normalized structure factors E_o and E_c, we get

$$X = 2D|E_c||E_o|/(1-D^2),$$

which, in the case of Gaussian distribution of errors $\Delta\mathbf{r}$, reduces to

$$\begin{aligned} X &= |E_c||E_o|/\sinh(2\pi^2\sigma^2H^2) \\ &= |E_c||E_o|/\sinh u^2, \end{aligned}$$

where

$$u^2 = 2\pi^2\sigma^2H^2.$$

Fig. 1 shows a family of curves for different values of W as a function of $|E_c||E_o|$ and $H\sigma$. For convenience these have been drawn similar to the figure in Vand & Pepinsky's paper (1957). It is clear that most of the discussions given by Vand & Pepinsky for the centrosymmetric case apply equally well to the non-centrosymmetric case, except that the nature of the expression for the weighting function W in the present case is different. Thus, the following few comments pertinent to the present case should suffice. Corresponding to the

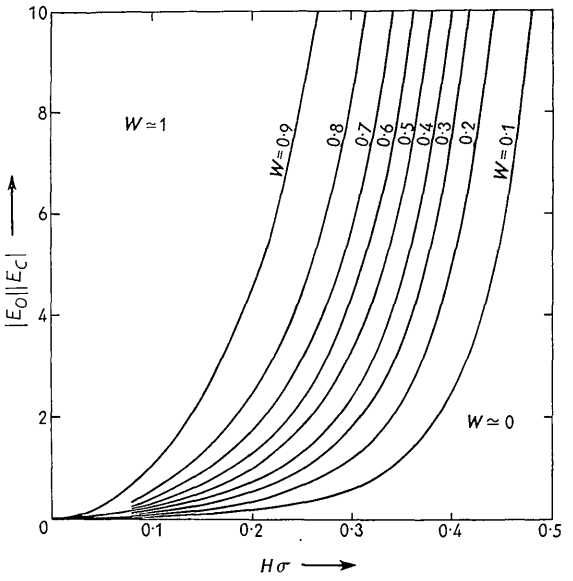

Fig. 1. Weighting function W plotted against $|E_o||E_c|$ and $H\sigma$.

equation (25) of Vand & Pepinsky the equation of the boundary at which $W=\frac{1}{2}$ is given in the non-centrosymmetric case by

$$|E_c||E_o| = 1.15 \sinh u^2,$$

which is thus only slightly different from the corresponding expression for the centrosymmetric case. Therefore, the practical criteria discussed by Vand & Pepinsky will also hold here. Finally, it may be added that unlike the direct analytical relation between R and D available for the centrosymmetric case (see expressions (26) and (30) of Vand & Pepinsky, 1957) it has not been possible to obtain such an explicit relation for the non-centrosymmetric case.

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Polarization factor for X-ray monochromator crystals.

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The present authors recently carried out an absolute intensity measurement of X-ray reflexions from magnesium oxide powders, with Cu $K\alpha$ radiation monochromated by a curved lithium fluoride crystal using the 200 reflexion. The structure amplitudes derived therefrom are hereafter denoted as $F_{A,K}$. By an independent measurement with filtered Cu $K\alpha$ and Cr $K\alpha$ radiations, the relative values of structure amplitudes, F_R, were also obtained. Although $F_{A,K}$ and F_R are the quantities which are expected to be proportional to each other, a characteristic discrepancy from the proportionality was found as shown in Fig. 1, where $\log(F_{A,K}/F_R)$ is plotted against the scattering angle 2θ.

Such an anomaly seems to be ascribed to a misuse, in deriving $F_{A,K}$, of the polarization factor

$$p_K = \frac{1+\cos^2 2\theta_M \cos^2 2\theta}{1+\cos^2 2\theta_M} \qquad (1)$$

where θ_M is the Bragg angle at the monochromator.

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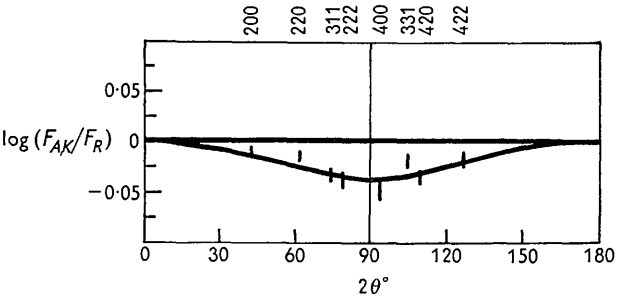

Fig. 1. $\log(F_{A,K}/F_F)$ against 2θ for magnesium oxide. $c=0{\cdot}6$.

The form (1) is valid when an ideally mosaic crystal is used as monochromator. If, however, the crystal is ideally perfect, we have to make use of the polarization factor

$$p_D = \frac{1+|\cos 2\theta_M|\cos^2 2\theta}{1+|\cos 2\theta_M|} \qquad (2)$$

(Kuriyama & Hosoya, 1963). In most cases the use of (1) may be approximately justifiable since monochromator